<Division of Materials Chemistry> Chemistry of Polymer Materials

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- Chemistry of Polymer Materials -

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Visitors

Prof MA, Yung-Dae	Dankook University, Korea, 27–29 April 2007
Prof BUBACK, Michael	University of Göttingen, Germany, 10–14 June 2007
Prof MATYJASZEWSKI, Krzysztof	Carnegie Mellon University, USA, 10–14 June 2007
Prof ZHAO, Bin	University of Tennessee, USA, 10–14 June 2007
Ms MACEWAN, Maura E	University of Virginia, USA, 19 June–21 August 2007

Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of concentrated polymer brushes (CPB).

Research Activities (Year 2007)

Publications

Fukuda T, Tsujii Y, Ohno K: Grafting and Polymer Brushes on Solid Surfaces; *In Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*, Wiley-*VCH*, 1137-1178 (2007).

Ohno K, Morinaga T, Takeno S, Tsujii Y, Fukuda K: Suspensions of Silica Particles Grafted with CPB: Effects of Graft Chain Length on Brush Layer Thickness and Colloidal Crystallization, *Macromolecules*, **40**, 9143–9150 (2007).

Goto A, Zushi H, Hirai N, Wakada T, Tsujii Y, Fukuda T: Living Radical Polymerizations with Ge, Sn, and P Catalysts - RTCPs, *J. Am . Chem. Soc*., **129**, 13347-13354 (2007).

Presentations

Tsujii Y, CPBs and Biointerfaces (invited): 29th Ann. Meeting of Jpn. Soc. Biomater. Osaka, 26–27 November 2007.

Fukuda T, New Development of CPBs (invited). And other 5 presentations: ICR Int. Symp. (ICRIS'07) Organized by Fukuda T, Kyoto, 11–13 June 2007.

15 Presentations, 56th Spring Meeting, Soc. Polym. Sci., Jpn., Kyoto, 29–31 May 2007.

10 Presentations, 56th Autumn Meeting, Soc. Polym. Sci., Jpn., Nagoya, 19–21 September 2007.

Grants

Fukuda T, Science and Technology of CPB, Grant-in-Aid for Specially Promoted Research, 1 April 2005–31 March 2009.

Tsujii Y, Creation of New Bio-Interfaces Based on CPB, Grant-in-Aid for Science Research (A), 1 April 2005–31 March 2008.

Thermo-responsive Lubrication of Concentrated Polymer Brushes in Water

Well-defined, concentrated poly(*N*-isopropylacrylamide) brushes were successfully fabricated on solid surfaces via surface-initiated atom transfer radical polymerization using a newly-designed immobilizable initiator. These brushes were demonstrated to be highly swollen, nearly to their full lengths $L_{c,w}$, in water at 5°C, gradually shrinking with increasing temperature down to an almost nonswollen state above 30°C. On the other hand, a dramatic change in frictional coefficient μ between brushes (more than 3 orders of magnitudes) was observed at around 30°C, below which it stayed at very low values (< 10^{-3}).

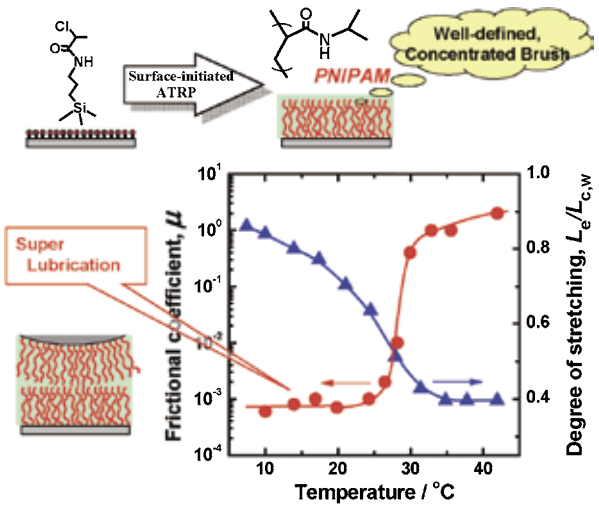

Figure 1. Swelling and frictional properties of concentrated PNIPAM brush in water.

Living Radical Polymerizations with Germanium, Tin, and Phosphorus Catalysts – Reversible Chain Transfer Catalyzed Polymerizations (RTCPs)

A novel class of living (controlled) radical polymerizations with germanium, tin, and phosphorus catalysts were developed. The polymerizations are based on a new mechanism, *Reversible chain Transfer (RT)* catalysis. Low-polydispersity polystyrene and polymethacrylates with predicted molecular weight were obtained with a fairly high conversion in a fairly short time. Attractive features of the catalysts include their *high reactivity*, *high solubility in organic media*, *insensitivity to air*, *minor color and smell*, *relatively low toxicity* (Ge and P catalysts), and *low cost* (P catalysts).

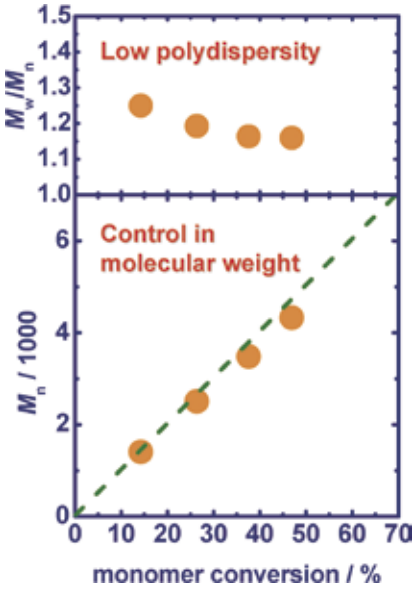

Figure 2. Plots of molecular weight (M_n) and molecular weight distribution (M_w/M_n) vs monomer conversion for the polymerization of styrene with GeI_4 (catalyst).

Tsujii Y, Patterning by Direct-Writing Graft Polymerization, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Tsujii Y, Development of Ionic-Liquid Polymer-Based Electrolyte Membrane by Controlled Graft Polymerization, Strategic Development of PEFC Technologies for Practical Application Program by NEDO, 9 December 2005–20 March 2008.

Tsujii Y, Development of Novel Lithium Ion Battery with Network Channel of High Ionic-Conductivity, Development of High-Performance Battery System for Next-Generation Vehicles by NEDO, 1 July 2007–20 March 2008.

Ohno K, Science of Semi-Soft Colloidal Crystals, Grant-in-Aid for Young Scientists (A), 1 April 2005–31 March 2008.

Ohno K, Fundamentals and Applications of Semi-Soft Colloidal Crystals, Industrial Technology Research Grant Program by NEDO, 1 January 2005–31 December 2007.

Goto A, Non-Transition-Metal Catalyzed and Photo-Induced LRPs, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Goto A, Development of Green LRP with Low Cost, Industrial Technology Research Grant Program by NEDO, 10 September 2007–31 August 2009.

Goto A, Fundamentals and Applications of Non-Transition-Metal Catalyzed LRP, Mitsubishi Chemical Corporation Fund, 1 November 2007–29 August 2008.